

(21) Application No 8011947
(22) Date of filing 10 Apr 1980
(30) Priority data
(31) 28966U

(32) 11 Apr 1979
(33) United States of America
(US)

(43) Application published
7 Jan 1981

(51) INT CL'
C08F 2/46
B05D 5/00
C08G 18/28 18/32 18/50
18/67 //
B32B 7/12 27/04 27/28
C07C 125/073
C09D 3/48

(52) Domestic classification
C3R 32D6A 32D6B
32D6C 32F5 32G2X 32G2Y
32H5B2 32H5BY 32H8
32J2F 32J2Y 32J3A 32J3Y
32KB 32KE 32KH 32T1
32T2X 33C 33P C10 C11
C12 C14A C14B C22 C25
L2CX L2X L3C L4F L5X
L6A L6D L6G
B2E 1739 1747 436T
443S 489T 491S 495T
623T M
B6N 0712 2704 2728
C2C 200 20Y 220 221 225
226 227 22Y 30Y 311 31Y
340 34Y 360 362 364 366
367 36Y 382 498 500 502
50Y 606 607 608 623 633
634 637 643 644 652 662
695 697 699 70Y 71Y 771
774 778 80Y 815 AA KA
WR WZ YA YB
C3P DF
C3Y B230 B240 B245
B262 B284 B286 F581
F582 G230 G320 H600
H620 H660

(56) Documents cited
None

(58) Field of search
C2C
C3P
C3R
C3V

(71) Applicants
Minnesota Mining and
Manufacturing Company,
3M Center, Saint Paul,
Minnesota 55101, United
States of America

(72) Inventors
Richard Graydon Newell
Stephen Franklin Wolf

(74) Agents
Lloyd Wise, Tregear & Co.

(54) Curable fluorocarbon substituted
polyetherurethaneacrylates

(57) Radiation polymerizable
compositions comprise
polyetherurethaneacrylates having
pendent fluorocarbon substituents.
The compositions may be radiation
polymerized, e.g. by electron beam,
actinic light or heat, to a light
transmissive material. The
fluorocarbon substituent generally has
the formula -W-R_n, wherein W is a
divalent connecting moiety and R_n is a
highly fluorinated, preferably
perfluorinated, aliphatic, aryl or alkaryl
radical. These compositions may be
utilized as 100% solids. The
compositions are particularly useful for
joining electro-optical components, and
as a protective coating.

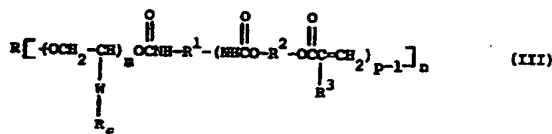
SPECIFICATION

Curable fluorocarbon substituted polyetherurethaneacrylates

This invention relates to compositions which are curable by radiation such as electron beam, actinic light or heat curable compositions. In one aspect, the present invention relates to polyetherurethaneacrylates. In a further aspect, the present invention relates to substituted polyetherurethaneacrylates and to the cured compositions produced therefrom. In yet a further aspect, this invention relates to fluorocarbon polyetherurethaneacrylates and to the radiation cured materials produced therefrom.

The advantages of radiation curable (especially actinic light curable) polymers, such as the ability to precisely control the time and extent of cure, increased shelf life and the utilization of undiluted (i.e., 100%) solids, has motivated considerable research effort toward the development of these compositions. The present invention is a novel radiation curable composition that is particularly useful for specialty applications, such as in joining electro-optical components, and as a protective coating.

In one aspect, the present invention provides polyetherurethaneacrylates having pendent fluorocarbon substituents. In a further aspect, the present invention provides radiation curable fluorocarbon - substituted polyetherurethaneacrylates having the formula:



wherein:

R is the residue or reaction product of a hydroxyl-containing material with an epoxy-containing material the hydroxyl-containing material having n hydroxyls;

n is an integer from 1 to 6 inclusively;

W is a polyvalent connecting moiety;

R_f is a monovalent highly fluorinated fluorocarbon radical;

m is a number having a value from about 1 to about 20;

R¹ is a polyvalent residue or reaction product of an organic polyisocyanate, R¹(NCO)_p (preferably a cycloaliphatic or aromatic polyisocyanate) and a hydroxyl-containing material, p having a value of 2 to 4;

R² is a divalent saturated aliphatic group having 2 to 6 carbon atoms and optionally one or two non-vicinal catenary oxygen atoms; and,

R³ is hydrogen or methyl.

The fluorocarbon-substituted polyetherurethaneacrylates (hereafter sometimes referred to as fluorocarbonetheracrylates in the interest of brevity) of this invention are curable (i.e., polymerizable) in the presence of catalysts or initiators which liberate or generate free-radicals under the influence of radiation such as actinic light or infrared radiation (heat). Free radicals can be generated in the system by the

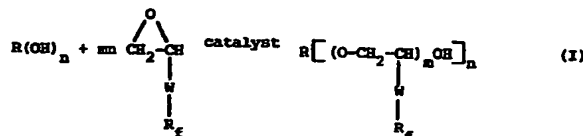
thermal or photo decomposition of known free radical initiators such as peroxides. Alternatively, the present materials have been found to be curable by the means of electron beam irradiation even in the complete absence of an initiator.

The cured materials of the invention can be utilized as tack-free protective coatings. Further, the cured compositions herein, having an optical transmission of greater than 95% and a low refractive index, are well suited for use as adhesives in applications where optical transmissivity is required. This utility is more completely described in assignee's copending application Serial No. 28,985 entitled "Coupling of Light Guides and Electro-optical Devices" filed in the name of James R. Onstott and Stephen F. Wolf, of even date herewith and incorporated by reference herein.

The fluorocarbon-substituted polyetherurethaneacrylates of this invention are generally prepared by procedures well known in the art. One synthetic route is as follows:

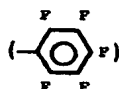
1. Preparation of a fluorocarbon-substituted polyetheralcohol (hereinafter sometimes designated fluorocarbonsalcohol or fluorocarbonpolyol).

A fluorocarbon-substituted (the substitution corresponding to -W-R_f in the final product) polyetheralcohol is prepared by ring opening addition polymerization of a fluorocarbon-substituted epoxide with a hydroxyl containing compound (containing n hydroxyl groups) initiator. This reaction may be written thus:



In I, R_f is a pendant, monovalent, highly fluorinated aliphatic, aryl, or alkaryl radical. "Pendent" as the term is used herein means not of the backbone carbon chain, i.e., non-catenary. By "highly fluorinated" is meant that generally 35 to 85 weight percent, preferably 50-77 weight percent, of the fluorocarbon radical is fluorine, with at least 75 percent of the non-catenary carbon valence bonds being attached to fluorine atoms. The weight percent of fluorine in the preferably saturated pendent fluorocarbon radical is found by dividing the total atomic weight of the radical into the total atomic weight of the fluorine atoms present in the radicals (e.g., -CF₃ is 82.6 weight percent fluorine). Where R_f contains a plurality of carbon atoms in a skeletal chain, such chain may be straight, branched or cyclic but preferably is straight. The skeletal chain of carbon atoms can be interrupted by divalent oxygen or trivalent nitrogen heteroatoms, each of which is bonded only to carbon atoms, but where such heteroatoms are present, it is preferable that the skeletal chain contain not more than one said heteroatom for every two carbon atoms. An occasional carbon-bonded hydrogen atom, bromine atom, or chlorine atom may be present. Where such atoms are present, they are preferably present to the extent of not more than one such atom for every two carbon atoms in the chain. Thus, the non-skeletal

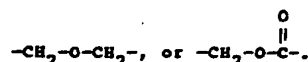
valence bonds are preferably carbon-to-fluorine bonds, that is, R_f is preferably perfluorinated. The total number of carbon atoms of R_f can vary and can be, for example 1 to 18, preferably 1 to 12. Where R_f is or contains a cyclic structure, such structure preferably has 5 or 6 ring member atoms, 1 or 2 of which can contain heteroatoms, e.g., oxygen and/or nitrogen. Where R_f is aryl, it has 1 or 2 rings. Where R_f is an aromatic structure, the aromatic structure may be substituted with lower alkyl radicals (i.e., alkyl radicals having 1-4 carbon atoms). Examples of such aryl radicals include perfluorophenyl



4-trifluoromethylphenyl, and perfluoronaphthyl. R_f is also preferably free of ethylenic or other carbon-to-carbon unsaturation, that is, it is a saturated aliphatic or heterocyclic radical. Examples of useful R_f radicals are fluorinated alkyl, e.g., $-CF_2$, $-C_2F_5$, and alkoxyalkyl, e.g., CF_3OCH_2 , said radicals being preferably perfluorinated straight-chain alkyl radicals, C_nF_{2n+1} , where n is 1 to 12.

In the above formula, W is a polyvalent connecting moiety. W has a valence of at least 2 and is preferably selected from the group consisting of carbon-

to-carbon single bonds,

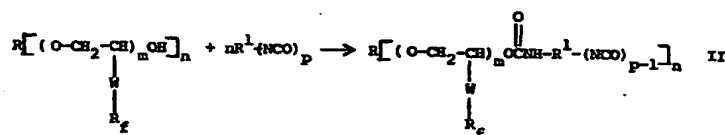


The pendent group $-W-R_f$ is herein sometimes referred to as "the pendent fluorocarbon substituent", or the "highly fluorinated fluorocarbon substituent". This latter term is used especially when $-W-R_f$ and $-R_f$ both are highly fluorinated.

In reaction I above, catalysts may be employed such as Lewis acids, optionally modified with organotin compounds. Generally, the reaction may be run without solvent at a temperature of about 25°C to 150°C. It is important to note at this juncture that the fluorocarbon substituent of the epoxide ($-W-R_f$ in I) becomes the pendent fluorocarbon-substituent of the novel polyetherurethaneacrylates of the invention. Hence, in this preparative route, the pendent fluorocarbon substituent of the end product is determined by the materials reacted in the first step.

II. Preparation of an isocyanate-terminated fluorocarbon-substituted polyether.

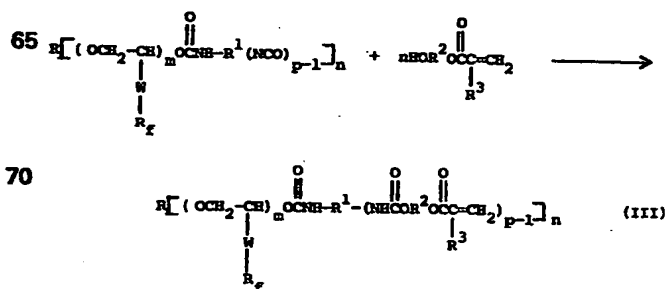
The product of Step I is reacted with an organic polyisocyanate $R'(NCO)_p$, p having a value of 2 to 4 according to the reaction:



Preparative Step II is generally discussed below.

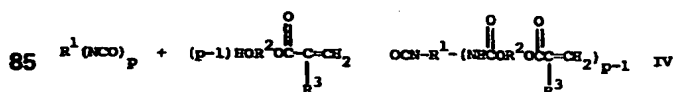
III. Preparation of the fluorocarbonacrylates. The novel fluorocarbon-substituted

polyetherurethaneacrylates are prepared by reacting the product of Step II with a hydroxyalkylacrylate according to the reaction:

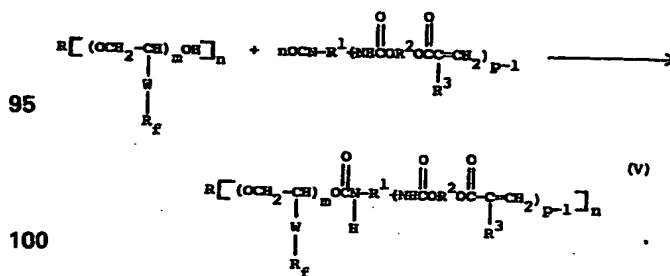


In the structural formulae of equations I, II and III, R , R_f , R^1 , R^2 , R^3 , m , n , p , and W are all defined as above.

In an alternative route, the fluorocarbonacrylates of the invention can be prepared by the reaction of a hydroxyalkylacrylate with an organic diisocyanate to form a polyisocyanatoalkylacrylate, viz.,



The product of IV may then be reacted with a fluorocarbon-substituted polyetheralcohol such as the product of I above. This reaction may be written as follows:



All symbols are defined as above.

It is also contemplated and often desirable to modify the fluorocarbon-substituted polyetheralcohols of Step I above, by copolymerizing the fluorocarbon epoxide with one or more oxacycloalkanes which may or may not have fluorine substituents.

Oxacycloalkanes (cyclic ethers) herein comprise cycloaliphatic hydrocarbons having at least one oxygen heteroatoms in the aliphatic ring. Oxacycloalkanes polymerize by ring opening to polyethers. Particularly useful oxacycloalkanes are the 2-, 3- and 4- carbon atom (which in conjunction with an oxygen heteroatom form 3-, 4- and 5- member rings) species known as oxiranes, oxetanes and oxolanes.

It has been found that the fluorocarbon-substituted polyether alcohols (Equation I) can be modified with up to about 80% by weight oxacycloalkanes which contain no fluorine.

5 Selectively incorporating oxacycloalkanes in the fluoropolyetherurethaneacrylates provides a method to control the optical characteristics of the finished polymer. For example, decreasing the fluorine content of the polymer by increasing the
10 amount of oxacycloalkane in the polyether chain, generally increases its refractive index.

Suitable hydroxyl-containing materials which can be used as initiators in step I preferably contain 1 to 6 hydroxyl groups and include water and monomeric
15 or polymeric aliphatic alcohols having 1 to 18 or more carbon atoms. Examples of such aliphatic alcohols include methanol, ethanol, 2-chloroethanol, isopropanol, octanol - 1, dodecanol, cyclohexanol, ethyleneglycol, propyleneglycol, 1,3-butanediol, 3,4-dibromo-1,4-butanediol, 1,4-butanediol, neopentylglycol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, 2-(2-hydroxyethoxy)ethanol, 2-[2-(hydroxyethoxy)ethoxy]ethanol, 2-[[2-(2-(hydroxyethoxy)ethoxy)ethoxy]]ethanol, 3-(3-hydroxypropoxy)propanol, glycerol, trimethylpropane, pentaerythritol, dipentaerythritol, sorbitol, 1,1,4,4-tetrahydroperfluorotetramethyleneglycol, 1,1,5,5-tetrahydroperfluoropentamethyleneglycol, and
30 1,1,6,6-tetrahydroperfluorohexamethyleneglycol, and the monomeric alcohols described in U.S. Patent 3,318,960. Preferred hydroxyl-containing materials for use as initiators are the short chain aliphatic terminal diols containing 4 to 6 methylene
35 groups such as 1,6-hexanediol and 1-4 butanediol.

Suitable polymeric aliphatic alcohols for use in the present invention generally contain only carbon, hydrogen and oxygen and have 1 to 6 hydroxyl groups. The hydroxyl groups may be primary or
40 secondary and generally should be present to the extent of about one per thousand units of molecular weight (i.e., a hydroxy equivalent weight of less than 1000 is preferred). Polymeric aliphatic alcohols having a hydroxyl equivalent weight of greater than
45 about 1000 generally produce polyetherurethaneacrylates having a fluorine content which is too low to exhibit the advantageous properties of the present materials. Polymeric diols and triols having a molecular weight of less than about 2000 (corresponding to a hydroxyl equivalent weight of 670 and 1000 for triols and diols respectively) constitute a preferred class of polymeric aliphatic alcohols.

Other useful polymeric aliphatic alcohols include polyester polyols, such as the lactone polyesters
55 described in U.S. Patent 3,169,945 (especially the polyesters terminated with two or more hydroxyl groups formed by reaction of epsilon-caprolactone and polyol), the hydroxyl-terminated polyester condensation polymers described in U.S. Patent
60 3,641,199, the substantially linear, saturated, hydroxyl-terminated polyesters described in U.S. Patent 3,457,326, the hydroxy-containing polyesters described in U.S. Patent 3,931,117, and the hydroxy-terminated block polymers of polyethers and polyesters described in U.S. Patent 3,960,572. Useful

polyether block polymers include the hydroxy-terminated polyether condensation polymers described in U.S. Patent 3,641,199, the substantially linear, saturated hydroxy-terminated polyethers described in U.S. Patent 3,457,326, the polyalkylene ether polyols described in U.S. Patents 3,499,852, 3,697,485 and 3,711,444, and the polyethylene glycol and polypropylene glycols described in U.S. Patent 3,850,770. Useful polyolefin polyols include those described in U.S. Patent 3,678,014 and the α,ω -diols from ethylene described in *J. Polymer Science*, Part A-1, Vol. 5, p. 2693 (1967). A particularly useful, commercially available class of caprolactone polyols which can be used are those sold under the
80 Trademark "NIAK," such as PCP-0200, PCP-0210, PCP-0230 and PCP-0300 (e.g., see technical bulletin F42464 of Union Carbide Corp.).

Other useful hydroxyl-containing materials which can be utilized as initiators in I include polysiloxane polyols such as the hydroxy-terminated diorgano-polysiloxanes described in U.S. Patents 4,098,742 and 3,886,885, and the siloxanes having a reactive hydroxyl-functional group bonded to at least two of its silicon atoms, described in U.S. Patents 3,577,264,
90 3,976,676 and 4,013,698.

Suitable epoxide-containing compounds having pendent highly fluorinated fluorocarbon substituents (which become W-R, in the finished polymer) are the fluoroaliphatic glycidyl ether compounds including perfluoroalkyl glycidyl ethers such as perfluoroisopropyl glycidyl ether whose preparation is described in U.S. Patent 3,361,685; the 1,1-trihydrofluoroalkyl glycidyl ethers such as the 1,1,3-trihydrotetrafluoroethyl glycidyl ether whose preparation is described in U.S. Patent 3,417,035; the 1,1-dihydroperfluoroalkyl glycidyl ethers such as 1,1-dihydrotrifluoroethyl glycidyl ether, 1,1-dihydro-pentafluoropropyl glycidyl ether, 1,1-dihydroheptafluorobutyl glycidyl ether, 1,1-dihydro-pentadecafluorooctyl glycidyl ether, 1,1-dihydroheptadecafluorononyl glycidyl ether and others whose preparation is described in U.S. Patent 3,591,547; and the glycidyl perfluoroalkanoates such as glycidyl perfluoroacetate, glycidyl perfluoropropionate, glycidyl
110 perfluorobutyrate, and glycidyl perfluorooctate which are prepared by the esterification reaction of glycidol and the corresponding perfluoroalkanoic acids and the glycidyl ethers of fluorinated phenols such as perfluorophenyl glycidyl ether and trifluoromethylphenyl glycidyl ether.

Examples of oxaheterocycles that can be copolymerized with the fluorocarbon substituted epoxides for preparing the fluorocarbon alcohols and polyols include ethylene oxide; alkyl-substituted
120 ethylene oxides, e.g., propyleneoxide, epichlorohydrin, butyleneoxide; alkenyl-substituted ethylene oxides, e.g. butenyloxy; aryl-substituted ethylene oxides, e.g., styreneoxide, benzylethylene oxide; glycidyl ethers, e.g., methyl glycidyl ether, butyl glycidyl ether, phenyl glycidyl ether, 3-phenylpropyl glycidyl ether, cyclohexyl glycidyl ether; cycloalkyl oxides, e.g., cyclohexene oxide, cyclopentene oxide and limonene oxide; oxetanes, e.g., oxetane and 2,2-dimethyl oxetane; and the oxolanes, e.g.,
130 tetrahydrofuran. Other suitable copolymerizable

epoxides and glycidyl ethers are disclosed in U.S. Patent 3,417,035 among others.

The preferred catalysts for preparing the fluorocarbon alcohols and polyols (I, above) are the catalyst systems comprising: (1) a fluorinated acid selected from bis(fluorinated aliphatic sulfonyl)alkanes, fluorinated aliphatic sulfonic acids, and Lewis acid of the formula $H_a \times F_{b+2}$ where X may be aluminium, boron, phosphorus, arsenic, tin, antimony and the like; b is the highest oxidation number of X and a is 0 or 1; and (2) a polyvalent tin compound as are taught in assignee's copending application SN 906,744, entitled "Colorless Hydroxyl-terminated Poly(chloroalkylene ethers)", filed on May 17, 1978 in the name of Chung I. Young and Loren I. Barber, Jr., incorporated herein by reference. Many other catalysts are useful for preparing the fluorocarbon alcohols by cationic polymerization techniques. Useful Lewis acid catalysts are disclosed in U.S. Patents 3,269,961; 3,850,856; 3,910,878; 3,910,879; and 3,980,579 among others. Useful aluminium alcoholate catalysts are disclosed in U.S. Patent 3,318,960 and the use of diethyl zinc to polymerize glycidyl ethers is disclosed in U.S. Patent 3,361,685.

The fluorocarbon alcohols are prepared in accordance with Equation I by adding one to 20 mole equivalents of fluorocarbon epoxy compound to one hydroxyl equivalent of hydroxyl-containing initiator compound. The temperature and time required for the reaction will vary depending on the particular reactants and amounts employed and on the nature and amount of catalyst used. Generally, temperatures from about 20°C to 200°C for periods up to 24 hours suffice for the reaction. The catalyst concentration for the preferred fluorinated acid/organo tin compound can be from about 0.1% to about 1% of the total weight of reactants. Generally, the higher the catalyst concentration, the lower the temperature and shorter the time required for the reaction. An inert organic solvent such as dichloromethane or chloroform may be employed to facilitate the reaction.

Polyisocyanates useful for preparing the fluorocarbon acrylates can be aliphatics, cycloaliphatic or aromatic. Exemplary diisocyanates are disclosed in U.S. Patents 3,641,199; 3,700,643; 3,960,572 and others. Preferred polyisocyanates are the cycloaliphatic and aromatic diisocyanates of which isophorone diisocyanate and toluene diisocyanate (tolylene - 2,4 - diisocyanate) are the most preferred.

An exemplary list of hydroxyalkylacrylates useful for preparing the polyetherurethaneacrylates is disclosed in U.S. Patent 3,577,262. Other desirable compounds include hydroxyalkylpolyacrylates such as trimethylolpropanediacrylate and pentaerythritoltriacylate.

The reaction of the fluorocarbon alcohol, diisocyanate, and hydroxyalkylacrylate to form the polyetherurethaneacrylate in accordance with Equations II and III or IV and V is performed in sequential steps at temperatures from about 20°C to 100°C for about 10 minutes to several hours, sufficient to bring about the reaction. Preferably, a tin catalyst such as

diphenyl dibutyl tin dilaurate is used to promote the reaction. Other suitable catalysts include compounds containing tertiary amino groups, and titanium compounds. Generally, the catalyst is included to the extent of about 0.1 to about 1.5 percent of the total weight of reactants.

Depending on the use to which the fluorocarbon acrylates are to be put, various materials can be added including curing catalysts, fillers, extenders, pigments and dyes.

Generally, diluent monomers are added to fluorocarbon-substituted polyetherurethaneacrylates of the invention to reduce their viscosity and increase or decrease their curing rate. Amounts of the diluent monomer up to 2 or more times the weight of the polyetherurethaneacrylate present may be employed. A suitable diluent monomer is any ethylenically unsaturated monomer that is compatible and copolymerizable with the polyetherurethaneacrylates of the invention. Suitable ethylenically unsaturated monomers include acrylic acid, acrylates and acrylate esters such as methyl methacrylate, ethyl acrylate, 2 - ethylhexyl acrylate, cyclohexyl acrylate, styrene and its derivatives such as, 2 - chlorostyrene, 2,4 - dichlorostyrene, acrylamide, acrylonitrile, *t* - butyl acrylate, methyl acrylate, butyl acrylate, 2 - (N - butylcarbamyl)ethyl methacrylate and 2 - (N - ethylcarbamyl)ethyl methacrylate, N - vinyl - 2 - pyrrolidone. Especially desirable diluent monomers are the acrylic acid and methacrylic acid esters of 1,1 - dihydroperfluoroalkanes such as 2,2,2 - trifluoroethyl acrylate, 1,1 - dihydroperfluoropropyl methacrylate, 1,1 - dihydroperfluorobutyl acrylate and 1,1 - dihydroperfluorooctyl methacrylate. Other diluent monomers that can be incorporated into the composition of the invention to increase the cross-link density include 1,4 - butylene dimethacrylate or acrylate, 1,1,6,6 - tetrahydroperfluorohexanediol diacrylate, ethylene dimethacrylate, glyceryl diacrylate or methacrylate, glyceryl triacrylate or trimethacrylate, pentaerythritol triacrylate or trimethacrylate, diallyl phthalate, dipentaerythritol pentaacrylate, neopentylglycol triacrylate and 1,3,5 - tri(2 - methacryloxyethyl) - s - triazine.

Suitable catalysts or initiators for use in polymerizing (curing) the compositions of the invention are catalysts which liberate or generate free-radicals upon addition of energy in the form of radiation such as heat, actinic light or electron beam. Such catalysts are well known and are described frequently in the polymerization art, e.g., Chapter II of "Photochemistry" by Calvert and Pitts, John Wiley & Sons (1966).

Included among free radical catalysts are the conventional heat activated catalysts such as organic peroxides and organic hydroperoxides; examples are benzoyl peroxide, tertiary-butyl perbenzoate, cumene hydroperoxide, azobis(isobutyronitrile) and the like. The preferred catalysts are photopolymerization initiators which facilitate polymerization when the composition is irradiated. Included among such initiators are acyloin and derivatives thereof, such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, and α - methylbenzoin; diketones such as ben-

zil and diacetyl, etc.; organic sulfides such as diphenyl monosulfide, diphenyl disulfide, decyl phenyl sulfide, and tetramethylthiuram monosulfide; S - acyl dithiocarbamates, such as S - benzoyl -

5 N,N - dimethyldithiocarbamate; phenones such as acetophenone, α,α,α - tribromacetophenone, α,α - diethoxyacetophenone, *o* - nitro - α,α,α - tribromoacetophenone; benzophenone, and *p,p'* - tetramethyldiaminobenzophenone; sulfonyl halides
10 such as *p* - toluenesulfonyl chloride, 1 - naphthalenesulfonyl chloride, 2 - naphthalenesulfonyl chloride, 1,3 - benzenedisulfonyl chloride, 2,4 - dinitrobenzenesulfonyl bromide and *p* - acetamidobenzenesulfonyl chloride. Normally, the initiator is used
15 in amounts ranging from about 0.01 to 5% by weight of the total polymerizable composition. When the quantity is less than 0.01% by weight, the polymerization rate becomes extremely low. If the initiator is used in excess of about 5% by weight, no correspondingly improved effect can be expected. Preferably, about 0.25 to 1.0% by weight of initiator is used in the polymerizable compositions. As noted above, a catalyst is not necessary when cure of the present materials is undertaken by such curing techniques as
20 electron beam.

The advantages and benefits of the compositions of the invention will be described in the following illustrative examples wherein the term "parts" refers to parts by weight unless otherwise indicated. In the
30 examples, the polyetherpolyols having pendent fluorocarbon groups were prepared according to the following general procedure.

The fluorocarbon alcohols were prepared in glass reaction flasks equipped with a stirrer, thermometer and a dropping funnel. A dry atmosphere was maintained within the flask during the reaction.

In each preparation, the hydroxyl-containing material (generally, about 0.1 mole) and 0.3 weight percent of a catalyst system of both bis(trifluoromethylsulfonyl) phenylmethane, $(\text{CF}_3\text{SO}_2)_2\text{CHC}_6\text{H}_5$, and dibutyldiphenyltin, $(\text{C}_4\text{H}_9)_2(\text{C}_6\text{H}_5)_2\text{Sn}$, were charged into the flask and heated to 80°C while stirring. The fluorocarbon epoxide and, where used, a copolymerizable oxacycloalkane (e.g., non-fluorine-containing oxirane, oxetane or oxolane) were then charged dropwise over a period of 0.5 to 1 hour to the stirred and heated flask. The resulting mixture was stirred at atmospheric pressure at 50°C to 125°C until the reaction was substantially complete, generally 8 to 24 hours. Then the reacted compositions were heated at about 80°C under about 0.5 Torr for a period of time sufficient to remove volatile components. The ratio of the moles of initiator hydroxyl compound to the moles of fluorocarbon epoxide and
55 oxacycloalkane (where used) was varied to control the hydroxyl equivalent of the product fluorocarbon alcohol.

EXAMPLES 1-21



In accordance with the general procedures given
60 above, various fluorocarbon alcohols were prepared. The initiator alcohol, fluorocarbon epoxide, mole ratio of alcohol to epoxide, reaction temperature and ratio of moles of bis(trifluoromethylsulfonyl)phenylmethane (commercially referred to
65 as phenyl disulfone, or ØDS) to moles of dibutyl-

diphenyltin in the catalyst system are given in Table I. Also given are the percent of epoxide conversion, the hydroxyl equivalent weight, the polydispersity (ρ = the ratio of weight average to number average molecular weight), and the values of *m* and *n* in the general formula of the product alcohol. Also given in Table I are the glass transition temperature, *T_g*, the melting point, *T_m*, and the refractive index of the product fluorocarbon alcohol.

75 The polydispersity was determined by gel permeation chromatography using a Waters, Associates chromatograph with a microstyrogel column. The hydroxy equivalent weights were obtained by reacting the hydroxyl group with phenylisocyanate, adding amine to remove the excess phenyl isocyanate and titrating the excess amine with dilute hydrochloric acid. The value of *m* was found by calculation from the hydroxy equivalent weight. The *T_g* and *T_m* were measured using differential thermal analysis (using the 900 DTA differential thermal-analyzer and instructions available from the E.I. duPont de Nemours and Company). The refractive indices were determined on a Karl Zeiss refractometer.

Table I

Fluorocarbon Alcohols $\text{R}[\text{OCH}_2\text{CH}_2\text{OH}]_n$ W
R₁

Exp. No.	Initiator Alcohol, R(OH) _n	W-R ₁	Initial mole ratio alcohol/epoxide	Reaction temp. (°C)	% epoxide Conversion	m	n	Oxydyl Equiv. Weight	T _g , °C	T _m , °C	Index N _D ²⁰	Ratio of σ_{DS} to $\sigma_{\text{Bu-Sir}}$
1	1,8 - hexanediol	-CH ₂ OCH ₂ C ₆ F ₁₃	1/2	80-100	99.8	1.0	3	524	1.04	-62 to -55	1.365	1/1
2	"	"	1/4	75	99.8	2.0	2	970	1.05	-54 to -43	1.358	1/1
3	"	"	1/5.8	80	94.5	2.8	2	1220	1.08	-44 to -34	—	1/1
4	"	"	1/12	75	88	5.3	2	2070	1.12	-33 to -23	1.3517	1/1
5	"	"	1/20	75	69	6.9	2	3200	1.11	-28 to -15	1.3502	1/1
6	1,4 - butanediol	"	1/4	80	100	2.1	2	987	1.05	-53 to -35	1.3549	1/1
7	tetraethyleneglycol	"	1/3.8	80	97.3	1.6	2	847	1.11	-51 to -43	1.380	1/1.5
8	1,4 - cyclohexane-dimethanol	"	1/4	CHCl ₃ reflux	100	1.4	2	717	1.04	-51 to -42	1.264	1/1.5
9	1,4 - cyclohexanediol	"	1/4	105-110	99	1.8	2	880	1.05	-42 to -32	1.256	1/2
10	1,1,6,6 - tetrahydroperfluorohexanediol	"	1/4.6	80	90	2.4	2	1226	1.32	-72 to -58	1.347	1/1.5
11	trimethylolpropane	"	1/8	85-90	100	2.2	3	1050	1.05	detectable	+2	1.355
12	1,2,6 - hexanetriol	"	1/8	80	99.9	1.9	3	920	1.07	not detectable	-3	1/2
13	"	-CH ₂ O  F	F 1/4	83	82	1.6	2	451	1.04	-45 to -40	1.465	1/1.5
14	"	-CH ₂ OCH ₂ (CF ₂) ₄ H	1/4	60-70 THF	—	1.8	2	737	1.02	-63 to -54	1.3726	1/1
15	allyl alcohol	-CH ₃	1/30	reflux	92.6	13.0	1	—	1.80	-74 to -84	1.440	1/1
16	1,8 - hexanediol	-CH ₂ OCH ₂ CF ₃	1/4	90	98.8	1.6	2	309	1.09	-66 to -58	1.406	1/1
17	"	-CH ₂ OC-F 	1/4	80	95	1.8	2	736	1.03	-22 to -14	1.381	1/1.1 ^b
18	"	1/1-CH ₂ CH ₂ -CH ₂ OCH ₂ C ₆ F ₁₃	1/4	80	97.6	1.9	2	555	1.04	-64 to -56	1.379	1/1.5
19	Carbowax 400 ^a	CH ₂ OCH ₂ C ₆ F ₁₃	1/2	90	92.5	2.0	2	1080	1.15	-56 to -47	1.372	1/1.1
20	Q4-3687 ^a	"	1/4	80-90	94.4	1.4	2	1240	—	-76 to -58	1.404	1/1.1
21	PCP-0200	"	1/4	80-90	99.9	2.0	2	1040	1.05	-64 to -53	1.381	1/1.1
										-41 to -30		

Notes

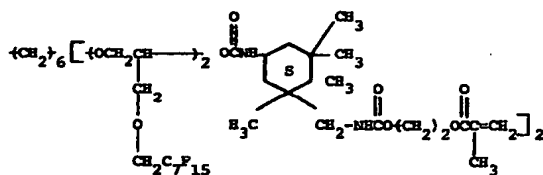
a. diphenyl dibutyltin

b. HSBF₃ · 6H₂O used in place of phenyl disulfone

The following additional examples illustrate the preparation of the fluorocarbon substituted polyetherurethane acrylates of the invention.

EXAMPLE 22

Thirty grams of the fluorocarbon polyol of Example 2 was mixed with one equivalent (7.50 g) of distilled isophorone diisocyanate until thoroughly blended. The mixture was roll milled until the infrared spectrum of the mixture was no longer attributable to hydroxyl functionality (about two hours). One equivalent (4.40 g) distilled 2-hydroxyethyl methacrylate was then added to the mixture and roll milling continued until the infrared spectrum no longer exhibited an absorption peak at 4.2 micrometers attributable to isocyanate functionality, but exhibited a peak at 5.84 micrometers attributable to urethane functionality (about two hours). The fluorocarbon etheracrylate obtained was clear, very viscous oil having a structure that was essentially:



To ten parts of the fluorocarbon etheracrylate obtained above was added and thoroughly mixed one part by weight of 1,1-dihydroperfluorooctyl methacrylate to reduce the viscosity of the mixture and 0.01 part of diethoxyacetophenone as actinic light or photoinitiator. The mixture was cast as a 140 micrometer thick layer between two sheets of 50 micrometer polyester. Upon exposure to the radiation from a xenon/mercury arc lamp, the layer cured within one minute to a tough, flexible, clear film having a refractive index of 1.402, a tensile strength of 85.4 kg/cm² (1200 psi), and an elongation at break of 9.4%.

EXAMPLES 23-25

The procedure of Example 22 was followed with the exception that different fluorocarbon polyols from Table 1 were employed. The results of these further runs are summarized in Table 2. Isophorone diisocyanate, 2-hydroxyethylmethacrylate, and diethoxyacetophenone photoinitiator were employed as in Example 22.

Table II**Properties of Cured Polymer**

Example Number	Fluorocarbon polyol used	Diluent monomer used	Refractive index, n_D^{22}	Tensile strength kg/cm ²	Elongation at break, %
23	Ex. 9	10% 1,1-dihydroxy perfluorooctyl methacrylate	1.395	145	14.4
24	Ex. 6	10% 1,1-dihydroxy perfluorooctyl methacrylate	1.411	155	40.8
25	Ex. 11	10% 1,1-dihydroxy perfluorooctyl methacrylate	1.397	77	6.7

EXAMPLES 26-29

The procedure of Example 22 was followed with the exception that the preparation of the highly fluorinated fluorocarbon substituted polyetherurethaneacrylate was accomplished by heating the reaction mixture with an infrared lamp on a roll mill. The results of these runs are summarized in Table III.

TABLE III

Properties of Cured Polymer

Example Number	Fluorocarbon polyol used	Diluent monomer used	Refractive index, n_D^{22}	Tensile strength, kg/cm^2	Elongation at break, %
26	Ex. 14	10% 1,1 - dihydroxy perfluorooctyl methacrylate	1.433	120	46.8
27	Ex. 3	10% 1,1 - dihydroxy perfluorooctyl methacrylate	1.398	41.3	27.6
28	Ex. 8	10% 1,1 - dihydroxy perfluorooctyl methacrylate	1.431	145	28
29	Ex. 2	none	1.402	20	12.8

EXAMPLE 30

A fluorocarbonpolyetherurethaneacrylate was prepared by mixing on a roller mill for about two hours a mixture of 20 parts of the fluorocarbon diol of Example 2 and 3.19 parts of isocyanatoethyl methacrylate (available from Dow Chemical Company). The resulting compound had an infrared absorption peak at 5.84 micrometers attributable to urethane functionality. A cured film prepared without addition of diluent monomer had a refractive index of 1.388, a tensile strength of 60 kg/cm^2 (850 psi) and an elongation at break of 2%.

EXAMPLE 31

Ten parts of fluorocarbonetheracrylate as described in Example 2 was diluted with 3 parts by weight of 1,1 - dihydroperfluorooctyl methacrylate and polymerized as a film that had an index of refraction of 1.408, a tensile strength of 133 kg/cm^2 (1900 psi) and an elongation at break of 36%.

EXAMPLE 32

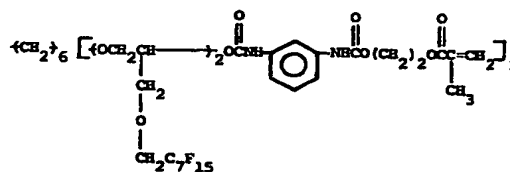
When ten parts of fluorocarbonetheracrylate as described in Example 22 were diluted with five parts by weight of 1,1 - dihydroperfluorooctyl methacrylate and polymerized, a film was obtained having an index of refraction of 1.397, a tensile strength of 78.4 kg/cm^2 (1120 psi) and an elongation at break of 82%.

EXAMPLE 33

The fluorocarbonetheracrylate prepared in Example 22 was diluted with 10% by weight of the acrylate ester rather than the methacrylate ester of 1,1 - dihydroperfluorooctyl alcohol and cast as a 140 micrometers thick film between two sheets of polyester film. The cured film obtained had a refractive index at 25°C of 1.413, a tensile strength of 78.4 kg/cm^2 (1120 psi) and an elongation at break of 29%.

EXAMPLE 34

The procedure of Example 22 was followed with the exception that an equivalent weight of tolylene - 2,4 - diisocyanate was used in place of isophoronedisocyanate. The fluorocarbonetheracrylate obtained had an infrared spectrum consistent with a structure that was essentially:



On polymerization of the fluorocarbonetheracrylate without use of a diluent monomer, a cured film having a refractive index at 25°C of 1.408, a tensile strength of 65 kg/cm^2 (928 psi), and an elongation at break of 42% was obtained.

EXAMPLE 36

A rapidly photocuring system comprising fluorocarbonetheracrylates was formulated by mixing 4 grams of the fluorocarbonetheracrylate as described in Example 2 with 2 grams of 1,1 - dihydroperfluorooctylacrylate, 2 grams of 1,6 - tetrahydroperfluorohexanediol diacrylate, 0.8 gram N - vinyl - 2 - pyrrolidone and 0.5 gram diethoxyacetophenone. This formulation was coated onto poly(vinylchloride) film. Upon exposure in air to ultraviolet radiation of 1 joule/ cm^2 from two 200-watt medium pressure Hanovia mercury lamps, the formulation cured in 0.5 second to form a clear tough coating.

EXAMPLE 37

A sample of the fluorocarbonetheracrylate system described in Example 22 was coated onto a sheet of 2 mil(50 micrometer) polyester film using a #14 wire-wound bar. A thin sheet of 0.5 mil polyimide was rolled over the coating with a printing roller. The sample was irradiated in an electron beam at 1.05 KV and 2.5 milliamps for 8 seconds. The coating was completely cured after this exposure.

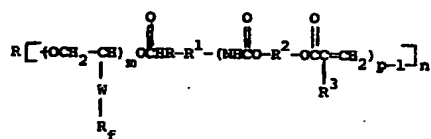
EXAMPLE 38

A 1-gram sample of the fluorocarbonetheracrylate system described in Example 22 was mixed with 25 mg AIBN (azobisisobutyronitrile) with gentle heating until the initiator was dissolved. A 5.4-mil (140-micrometer) coating was cast between two layers of 2-mil (50-micrometer) polyester. The sample was cured at 65°C for 15 hours, after which time the sam-

ple was cured.

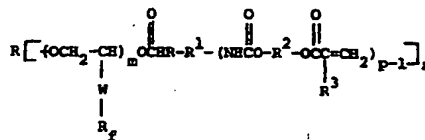
CLAIMS

1. A radiation curable composition comprising polyetherurethaneacrylate having pendent fluorocarbon substituents.
2. A composition according to claim 1 wherein said pendent fluorocarbon substituted is perfluorinated.
3. A composition according to claim 1 wherein said pendent fluorocarbon group has the formula $-W-R_1$, where $-W-$ is a polyvalent connecting moiety, and $-R_1$ is a monovalent highly fluorinated fluorocarbon radical.
4. A composition according to claim 3 wherein $-R_1$ is perfluorinated.
5. A composition which in admixture with a sufficient quantity of an actinic light activatable free-radical polymerization initiator is capable of being polymerized by actinic light, the composition comprising polyetherurethaneacrylate having pendent fluorocarbon substituents.
6. A composition according to claim 5 wherein said pendent fluorocarbon substituent is perfluorinated.
7. A composition according to claim 5 wherein said pendent fluorocarbon substituent has the formula $-W-R_1$, where $-W-$ is a polyvalent connecting moiety, and $-R_1$ is a monovalent highly fluorinated fluorocarbon radical.
8. A composition according to Claim 5 which further comprises an oxycycloalkane.
9. A composition according to Claim 5 wherein the polyetherurethaneacrylate has the formula



40 wherein:

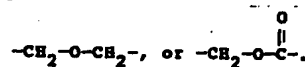
- R is the residue or reaction product of a hydroxyl-containing material having n hydroxyls the hydroxyl-containing material having been reacted with an epoxy-containing material;
- n is an integer from 1 to 6 inclusively;
- W is a polyvalent connecting moiety;
- R_1 is a monovalent highly fluorinated, fluorocarbon group;
- m is a number having a value from 1 to about 20;
- R^1 is a polyvalent residue or reaction product of an organic polyisocyanate, $R^1(\text{NCO})_p$, and a hydroxyl-containing material, p having a value of 2 to 4;
- R^2 is a divalent saturated aliphatic group having 2 to 6 carbon atoms and optionally one or two non-vicinal catenary oxygen atoms; and,
- R^3 is hydrogen or methyl.
10. A composition according to claim 5 which further includes an actinic light activatable free-radical polymerization initiator.
11. A composition according to claim 10 wherein said initiator comprises diethoxyacetophenone.
12. A radiation cureable composition comprising polyetherurethaneacrylate having pendent highly fluorinated fluorocarbon substituents, the composition having the formula:



70

wherein:

- R is the residue or reaction product of a hydroxyl-containing material having n hydroxyls the hydroxyl-containing material having been reacted with an epoxy-containing material;
- n is an integer from 1 to 6 inclusively;
- W is a polyvalent connecting moiety;
- R_1 is a monovalent highly fluorinated, fluorocarbon group;
- m is a number having a value from 1 to about 20;
- R^1 is a polyvalent residue or reaction product of an organic diisocyanate, $R^1(\text{NCO})_p$, and a hydroxyl-containing material, p having a value of 2 to 4;
- R^2 is a divalent saturated aliphatic group having 2 to 6 carbon atoms and optionally one or two non-vicinal catenary oxygen atoms; and,
- R^3 is hydrogen or methyl.
13. A composition according to claim 12 wherein said hydroxyl containing material comprising aliphatic alcohols having 1 to 18 carbon atoms and 1 to 6 hydroxyl groups.
14. A composition according to Claim 13 wherein said alcohols are 1,6 - hexanediol and 1,4 - butanediol.
15. A composition according to Claim 12 wherein said organic diisocyanate is cycloaliphatic.
16. A composition according to Claim 15 wherein said diisocyanate is isophorone diisocyanate.
17. A composition according to Claim 12 wherein said organic diisocyanate is aromatic.
18. A composition according to Claim 17 wherein the diisocyanate is toluene diisocyanate.
19. A composition according to claim 12 which further includes an actinic light activatable free-radical polymerization initiator.
20. A composition according to claim 19 wherein said initiator is diethoxyacetophenone.
21. A composition according to claim 12 wherein R_1 is selected from the group consisting of fluorinated alkyl, alkoxyalkyl, or perfluoroalkyl having a formula C_nF_{2n+1} , wherein n has a value of from 1 to 12.
22. A composition according to claim 12 wherein W is selected from the group consisting of carbon to carbon, single bond,



23. A composition according to Claim 12 which further comprises ethylenically unsaturated diluting monomers.
24. A radiation curable composition as claimed in Claim 1 substantially as herein described with reference to any one of the Examples.